PATENT SPECIFICATION (11) 1220069

1220069

NO DRAWINGS

(21) Application No. 56364/67 (22) Filed 12 Dec. 1967

(31) Convention Application No. 601330 (32) Filed 13 Dec. 1966

(33) United States of America (US)

(45) Complete Specification published 20 Jan. 1971

(51) International Classification

C08 41/0
C11d 17/04

(52) Index at acceptance

C3R 22A 22C1 22C11 22C12 22C13M 22C13S 22C14B 22C19 22C21 22C29 22C2A 22C33B 22C4 22C5B1 22C5B2 22C6X 22D1B1 22D2A1 22L1B 22L2B 22L2CX 22L4D 22T2

C5D 6A10 6B11B 6B12A 6B12B3 6B12E 6B12F1 6B12G2A 6B12G4 6B12K1 6B12L 6B12N2 6B12P 6B13 6B4 6B6 6C4 6C5 6C9

(54) IMPROVEMENTS IN OR RELATING TO A

ERRATUM

SPECIFICATION No. 1,220,069

Page 1, Heading, International Classification, *for* "C08 41/0" *read* "C08G 41/02"

THE PATENT OFFICE
23rd February 1971

duct of a polymeric fatty acid and a polyamine and, 1 to 95% by weight of a diethanolamide of a fatty acid having 6 to 12 carbon atoms.

The polyamide resin is a solid and is composed primarily of polyamides of molecular weight or weights within the range from 2000 to 10,000. Typical families of such polyamide resins are commercially available under such trademarks as VERSAMID. VERSALON, and EMEREZ. These solid resins may be compounded with similar polyamides which are liquid (including "semi-liquid" or "semi-solid") at room temperatures, in the range of molecular weights of from 600 to 800. The amount of the latter is sufficiently low to give a solid product.

These resins are of the general type of polyamides which are commercially available,

fatty acids we of course mean to include saturated fatty acids, unsaturated fatty acids, and branched chain fatty acids. Typical acids which are suitable include lauric, myristic, and any of those which are found in the so-called "coco" fatty acids.

The amount of polyamide present, based on the final product, may vary widely, e.g., from 5 to 95% by weight, with the amount of diethanolamide also varying widely, e.g., from 1 to 95%, and preferably from 5 to 40% by weight.

Detergent systems prepared from the foregoing components may readily be made in the form of washing bars or soft gels. The bars are hydrophilic gels and exhibit highly desirable washing characteristics. See, e.g., Examples 1, 2, 4, 6, 8—11, 15 and 16.

We have also found that into the foregoing

[Pri

SEE ERRATA SLIP ATTACHED

PATENT SPECIFICATION (11) 1 220 069

1 220 069

NO DRAWINGS

(21) Application No. 56364/67 (22) Filed 12 Dec. 1967

(31) Convention Application No. 601330 (32) Filed 13 Dec. 1966

(33) United States of America (US)

(45) Complete Specification published 20 Jan. 1971

(51) International Classification

C 08 41/0
C 11 d 17/04

(52) Index at acceptance

C3R 22A 22C1 22C11 22C12 22C13M 22C13S 22C14B 22C19 22C21 22C29 22C2A 22C33B 22C4 22C5B1 22C5B2 22C6X 22D1B1 22D2A1 22L1B 22L2B 22L2CX 22L4D 22T2

C5D 6A10 6B11B 6B12A 6B12B3 6B12E 6B12F1 6B12G2A 6B12G4 6B12K1 6B12L 6B12N2 6B12P 6B13 6B4 6B6 6C4 6C5 6C9

(54) IMPROVEMENTS IN OR RELATING TO A HYDROPHILIC GEL

(71) We, HAROLD SAMUEL AKRONGLOD, of 39, Cathay Road, East Rockaway, Long Island, New York, United States of America, ROCHELLE AKRONGOLD, of 39 Cathay Road, East Rockaway, Long Island, New York, United States of America, both citizens of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In its broadest aspect, our invention is concerned with a hydrophilic gel. These gels may be transparent, translucent, or opaque as desired.

According to the present invention, there is provided a hydrophilic gel consisting essentially of 5 to 95% by weight of a solid polyamide resin consisting of the reaction product of a polymeric fatty acid and a polyamine and, 1 to 95% by weight of a diethanolamide of a fatty acid having 6 to 12 carbon atoms.

The polyamide resin is a solid and is composed primarily of polyamides of molecular weight or weights within the range from 2000 to 10,000. Typical families of such polyamide resins are commercially available under such trademarks as VERSAMID, VERSALON, and EMEREZ. These solid resins may be compounded with similar polyamides which are liquid (including "semi-liquid" or "semi-solid") at room temperatures, in the range of molecular weights of from 600 to 800. The amount of the latter is sufficiently low to give a solid product.

These resins are of the general type of polyamides which are commercially available, e.g., under the trade mark Versamid (General Mills).

"Versamid" polyamide resins are identified as thermoplastic condensation products of polymerized linoleic acid with polyamine compounds such as ethylene diamine and diethylene triamine. Polyamide, resins of molecular weights in the range 6,000—9,000 have been found particularly advantageous for the present invention. These resins are commercially available in hard, brittle resin (#900) of softening point according to ASTM E-28 180—190°C., tough flexible resins (#930 and 940) softening points according to ASTM E-28 105—115°C., and even softer products of lower melting points.

The fatty acids used in preparing the diethanolamide are those containing from 6 to 12 carbon atoms, and preferably are those containing from 8 to 12 carbon atoms. By fatty acids we of course mean to include saturated fatty acids, unsaturated fatty acids, and branched chain fatty acids. Typical acids which are suitable include lauric, myristic, and any of those which are found in the so-called "coco" fatty acids.

The amount of polyamide present, based on the final product, may vary widely, e.g., from 5 to 95% by weight, with the amount of diethanolamide also varying widely, e.g., from 1 to 95%, and preferably from 5 to 40% by weight.

Detergent systems prepared from the foregoing components may readily be made in the form of washing bars or soft gels. The bars are hydrophilic gels and exhibit highly desirable washing characteristics. See, e.g., Examples 1, 2, 4, 6, 8—11, 15 and 16.

We have also found that into the foregoing

[Pric

SEE ERRATA SLIP ATTACHED

system there can be added useful and desirable compounds without affecting the clarity. That is, a transparent bar prepared from components of the foregoing type will retain its transparency even upon the incorporation therein of such washing compounds as, e.g. anionic surfactants such as triethanolamine lauryl sulphate, diethanolamine lauryl sulphate, various alkylaryl sulphonates, and triethanolamine stearate, sarcosinates, and protein based surfactants; nonionic surfactants such as e.g., the ethoxylated octyl and nonyl phenols; cationic surfactants such as dimethyl aminopropyl oleamide; or anphoteric surfactants, a suitable material being available under the trade mark "Miranol C_2M". See, e.g., Examples 1, 2 and 7. The amount of surfactant that may be so added to our polyamide-diethanolamide system may vary widely, e.g., from 5 to 75% by weight of the final product.

Additionally, we have found that a minor proportion of a metal soap (sodium stearate) can be added to our polyamide-diethanolamide system giving a resulting product which in its aesthetic and washing properties resembles the conventional transparent soaps based on glycerine. These washing bars are transparent, translucent, or opaque and the general slip and washing feel are that of soap. See, e.g., Example 3. The amount of soap which can be incorporated into the above system may be as little as desired, e.g. 0.1%, or more by weight of the finished product. Of course, as the amount of soap incorporated increases, the optical properties of the finished product gradually change from transparent to translucent to opaque.

It is of course frequently desirable to incorporate oils into our washing systems to serve as fatting or emollient agents. We have discovered that this can readily be done. For instance, when a cationic surfactant such as dimethyl aminopropyl oleamide is incorporated in our system, the system is then rendered compatible with fatting agents such as, e.g., mineral oil, isopropyl myristate or lanolin and the resultant product retains its initial transparency, translucence, or opaqueness.

An alternative means of rendering our washing system compatible to oils is by the expedient of adding thereto a branched chain fatty acid, e.g., isostearic acid. Of cours, the amount of branched chain fatty acid so added will vary, depending upon the amount of oil that is to be incorporated. See, e.g., Example 5. Typically the amount of such acid will be from 1 to 25 weight per cent of the finished composition, and the amount of oil may be from 1 to 50% by weight of the finished composition.

We have also found that if the polyamide is pretreated with n-propyl alcohol and thereafter the diethanolamide is added, the resulting gel exhibits a greater degree of softness as well as improved washing characteristics. By contrast, a firmer bar is obtained when the alcohol is added after admixing the polyamide and diethanolamide. The amount of n-propyl alcohol employed may be from about 0.1 to 50% by weight of the finished composition.

We have found that we can alter the physical and chemical properties of these washing bars or washing oil bars by addition and treatment with various additives. For instance, the hardness of the bar can be adjusted by appropriate addition to the polyamide-diethanolamide system of a dimerized fatty acid such as that sold under the trade mark Empol 1014, which is a C_{36} aliphatic dibasic acid containing 95% dimer acid, 4% trimer acid and 1% mono-basic acids in an amount of typically from 0.1 to 20% by weight of the finished bar. See, e.g., Example 6.

We have additionally discovered that if the polyamide is pre-treated (prior to addition of diethanolamide) with other polymeric materials such as, e.g., polyvinyl pyrrolidone, methyl cellulose or acrylamide-acrylic acid copolymer, one obtains gels having novel and unique properties. For instance, if the polyamide is pre-treated with an alkaline material such as triethanolamine the resulting polymer is more receptive to subsequent chemical treatment with a diethanolamide, thereby giving a product of altered nature, e.g., greater hardness. See Example 12. On the other hand, if polyvinyl pyrrolidone is employed in the pretreatment, the resulting gel exhibits marked adhesiveness (Example 13). By contrast, if methyl cellulose is used on the pre-treatment, one obtains a product which is highly soluble for machine washings, tends to disinfect and imparts an excellent softness of hand to woollens and cottens. Alternatively, if an acrylamide - acrylonitrile copolymer is employed for the pre-treatment, there results a bar having unusual resistance to crumbling.

We have also found that we can obtain a firmer and longer lasting bar by the simple excipient of pre-treating the polyamide resin with either sulphuric acid or hydrogen peroxide and thereafter treating the resulting product with diethanolamide. Thus, upon pretreating a polyamide, said Versamid 930, (see Table 28 of "Polyamide Resins", 2nd edition, by D. C. Floyd, published by Reinhold Publishing Corporation, New York, in 1966) with 0.1 normal sulphuric acid solution for 3 to 4 hours, and subsequently adding to the resulting product a diethanolamide of a fatty acid, there results an unusually firm and long lasting bar. Similar results are obtained if the polyamide is pretreated with a 1% by weight hydrogen peroxide solution. (See Example 14).

According to another embodiment of our invention, these compositions may be readily modified so as to exhibit antiseptic properties, as by the introduction of a halogen, prefer-

Thereafter the mixture is cooled to 65°C and 30 parts of n-propyl alcohol is added. The resulting product is a transparent bar which is an excellent cleaning product into which may also be incorporated, if desired, cationic surfactants such as dimethyl aminopropyl oleamide.

EXAMPLE 8

50 parts of polyamide (trade mark Versamid XR 1635) and 48.4 parts of diethanolamide of mixed fatty acids (trade mark Superamid GR) are heated at 70°C for one-half hour. Thereafter the temperature is raised to 85°C, and 1.6 parts of citric acid is added, and the whole is maintained at 85°C for 1 hour. The resultant product is a transparent bar.

EXAMPLE 9

20 parts of polyamide (trade mark Emerez 1535) and 70 parts of diethanolamide of mixed fatty acids (trade mark Schercomid CDO) are heated at 85°C for one-half hour. Thereafter 10 parts of oleic acid is added and the entire mixture is maintained at 85°C for 1 hour. The resulting transparent washing bar has a definite emollient or "greasy" feel.

EXAMPLE 10

60 parts of polyamide (trade mark Versamid 710) and 18 parts of diethanolamide of lauric acid (trade mark Foamole L) are heated at 85°C for 30 minutes. The temperature is then lowered to 70°C and 20 parts of n-propyl alcohol is added, and the entire mixture is permitted to stand for 10 minutes at 70°C. Thereafter 2 parts of citric acid is added, and the complete mixture stands for an additional hour at 70°C. The resulting transparent bar is excellent for metal cleaning.

EXAMPLE 11

15 parts of polyamide (trade mark Versamid 940) and 15 parts of diethanolamide of mixed fatty acids (trade mark Schercomid CDO) are heated at 85°C for 30 minutes. The temperature is then lowered to 70°C and 15 parts of n-propyl alcohol is added, and the mixture is permitted to stand for an additional hour at 70°C. Thereafter 20 parts of oleic acid is added and the mixture is permitted to stand for an additional hour. The resulting translucent product is an excellent general-purpose washing bar with an emollient feel.

EXAMPLE 12

50 parts of polyamide (trade mark Sun-Kem Nylon 543) and 3.5 parts of triethanolamine are heated at 85°C for 30 minutes. Then 46.5 parts of diethanolamide of mixed fatty acids (trade mark Superamid GR) (previously heated to 95°C) is added and the entire mixture is brought to 95°C and maintained at this temperature for 60 minutes. The resultant transparent bar is characterized by greater hardness and dirt-removing ability.

It should be noted that with respect to the foregoing example, if instead of trethanolamine is added after the Sun-Kem Nylon 543 and Superamid GR have been heated, then a somewhat softer bar results.

EXAMPLE 13

90 parts of polyamide resin (trade mark Emerez 150) is treated with 10 parts of polyvinyl pyrrolidone, having a molecular weight of 30,000 by heating to 75°C for 30 minutes, at which point there is added 90 parts of diethanolamide of lauric acid (trade mark Foamole L). The resultant solid transparent product exhibits marked adhesive properties and may be used in a wide variety of applications, e.g., in the preparation of a corn plaster.

EXAMPLE 14

90 parts polyamide (trade mark Versamid 930) are pre-treated with 10 parts of a 10% solution of 0.1 N sulphuric acid for 3 to 4 hours at 65°C and then the resulting product is admixed with 60 parts of diethanolamide of mixed fatty acids (trade mark Schercomid CDO). The resultant solid transparent product is much harder and longer lasting than a similar bar made without the sulfuric acid pre-treatment.

Similar results are obtained if instead of employing sulphuric acid for the pre-treatment there is instead substituted a 1% by weight hydrogen peroxide solution.

EXAMPLE 15

The procedure described in Example 2 is repeated, however, at 70°C. There is added 0.5 part iodine crystals. The resulting transparent bar is transparent and has a yellowish tint. It has excellent antiseptic properties yet is perfectly safe.

EXAMPLE 16

This illustrates the converting of a transparent bar to an opaque bar. 20 parts diethanolamide of mixed fatty acids (trade mark Schercomid CDO Extra) are heated to 85°C 28 parts polyamide (trade mark Versamid XR 1635) are added over an 8 to 10 minute interval until a homogeneous liquid is formed, to which 35 parts of trethanolamine lauryl sulphate (trade mark Maprofix TLS 65), 12 parts of diethanolamine lauryl sulphate (trade mark Maprofix 2109) and 0.07 part ethylene diamine tetraacetic acid (trade mark Sequestrene AA) are added, and the mixture is then cooled to 65°C. 5 parts n-propyl alcohol are then added and the mixture is cooled to 60°C and poured into an appropriately shaped mold. To this composition, which is still transparent, 8 parts of vinyl pyrrolidone-styrene

Thereafter the mixture is cooled to 65°C and 30 parts of n-propyl alcohol is added. The resulting product is a transparent bar which is an excellent cleaning product into which may also be incorporated, if desired, cationic surfactants such as dimethyl aminopropyl oleamide.

EXAMPLE 8

50 parts of polyamide (trade mark Versamid XR 1635) and 48.4 parts of diethanolamide of mixed fatty acids (trade mark Superamid GR) are heated at 70°C for one-half hour. Thereafter the temperature is raised to 85°C, and 1.6 parts of citric acid is added, and the whole is maintained at 85°C for 1 hour. The resultant product is a transparent bar.

EXAMPLE 9

20 parts of polyamide (trade mark Emerez 1535) and 70 parts of diethanolamide of mixed fatty acids (trade mark Schercomid CDO) are heated at 85°C for one-half hour. Thereafter 10 parts of oleic acid is added and the entire mixture is maintained at 85°C for 1 hour. The resulting transparent washing bar has a definite emollient or "greasy" feel.

EXAMPLE 10

60 parts of polyamide (trade mark Versamid 710) and 18 parts of diethanolamide of lauric acid (trade mark Foamole L) are heated at 85°C for 30 minutes. The temperature is then lowered to 70°C and 20 parts of n-propyl alcohol is added, and the entire mixture is permitted to stand for 10 minutes at 70°C. Thereafter 2 parts of citric acid is added, and the complete mixture stands for an additional hour at 70°C. The resulting transparent bar is excellent for metal cleaning.

EXAMPLE 11

15 parts of polyamide (trade mark Versamid 940) and 15 parts of diethanolamide of mixed fatty acids (trade mark Schercomid CDO) are heated at 85°C for 30 minutes. The temperature is then lowered to 70°C and 15 parts of n-propyl alcohol is added, and the mixture is permitted to stand for an additional hour at 70°C. Thereafter 20 parts of oleic acid is added and the mixture is permitted to stand for an additional hour. The resulting translucent product is an excellent general-purpose washing bar with an emollient feel.

EXAMPLE 12

50 parts of polyamide (trade mark Sun-Kem Nylon 543) and 3.5 parts of triethanolamine are heated at 85°C for 30 minutes. Then 46.5 parts of diethanolamide of mixed fatty acids (trade mark Superamid GR) (previously heated to 95°C) is added and the entire mixture is brought to 95°C and maintained at this temperature for 60 minutes. The resultant transparent bar is characterized by greater hardness and dirt-removing ability.

It should be noted that with respect to the foregoing example, if instead of trethanolamine is added after the Sun-Kem Nylon 543 and Superamid GR have been heated, then a somewhat softer bar results.

EXAMPLE 13

90 parts of polyamide resin (trade mark Emerez 150) is treated with 10 parts of polyvinyl pyrrolidone, having a molecular weight of 30,000 by heating to 75°C for 30 minutes, at which point there is added 90 parts of diethanolamide of lauric acid (trade mark Foamole L). The resultant solid transparent product exhibits marked adhesive properties and may be used in a wide variety of applications, e.g., in the preparation of a corn plaster.

EXAMPLE 14

90 parts polyamide (trade mark Versamid 930) are pre-treated with 10 parts of a 10% solution of 0.1 N sulphuric acid for 3 to 4 hours at 65°C and then the resulting product is admixed with 60 parts of diethanolamide of mixed fatty acids (trade mark Schercomid CDO). The resultant solid transparent product is much harder and longer lasting than a similar bar made without the sulfuric acid pre-treatment.

Similar results are obtained if instead of employing sulphuric acid for the pre-treatment there is instead substituted a 1% by weight hydrogen peroxide solution.

EXAMPLE 15

The procedure described in Example 2 is repeated, however, at 70°C. There is added 0.5 part iodine crystals. The resulting transparent bar is transparent and has a yellowish tint. It has excellent antiseptic properties yet is perfectly safe.

EXAMPLE 16

This illustrates the converting of a transparent bar to an opaque bar. 20 parts diethanolamide of mixed fatty acids (trade mark Schercomid CDO Extra) are heated to 85°C 28 parts polyamide (trade mark Versamid XR 1635) are added over an 8 to 10 minute interval until a homogeneous liquid is formed, to which 35 parts of trethanolamine lauryl sulphate (trade mark Maprofix TLS 65), 12 parts of diethanolamine lauryl sulphate (trade mark Maprofix 2109) and 0.07 part ethylene diamine tetraacetic acid (trade mark Sequestrene AA) are added, and the mixture is then cooled to 65°C. 5 parts n-propyl alcohol are then added and the mixture is cooled to 60°C and poured into an appropriately shaped mold. To this composition, which is still transparent, 8 parts of vinyl pyrrolidone-styrene